NASA TT F-10,869

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N67-25804

FACILITY FORM 602

(ACCESSION NUMBER)   (THRU)

(PAGES)   (CODE)

(NASA CR OR TMX OR AD NUMBER)   (CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546   APRIL 1967

VAPOR PRESSURE OF URANIUM MONOCARBIDE

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ABSTRACT. The partial vapor pressures of uranium and carbon over uranium moncarbide have been studied in the temperature range 1900-2400°K by a differential Knudsen method. The following equations were obtained for the temperature dependences of the vapor pressures (mm Hg):

$$\log p_U = 10.054 - \frac{2.809 \times 10^4}{T}$$

$$\log p_C = 2.515 - \frac{1.324 \times 10^4}{T}$$

The partial heat of sublimation of uranium $(\overline{\Delta H}_{298})$ assessed by the second- and third-law methods was 132.6 and 123 kcal/mol respectively. Up to a temperature of ~ 2100°K mainly carbon atoms vaporized, and above this temperature uranium atoms.

References 1-3 are concerned with the investigation of the vaporization /360* of uranium monocarbide and the results obtained in these references are presented in table 1. These data differ appreciably from one another. It is difficult to analyze the results given in references 2 and 3 because the papers presented at the Harwell symposium on carbides, as a rule, did not specify the details of the experimental methods. In view of the increased interest in uranium monocarbide it appeared expedient to refine the existing information on the vapor pressure of this compound, to determine the partial heats of sublimation and other thermodynamic characteristics.

We investigated the vaporization of uranium monocarbide using the Knudsen differential method (ref. 4) in the temperature range 1900-2400°K. For the initial compounds we used two series of specimens (I and II) prepared by a three-stage synthesis of uranium powders and carbon in vacuum at a pressure of 10^{-5}-5×10^{-6} mm Hg (950°C--2 hours; 1250°C--3 hours; 1650-1700°C--4 hours).

Specimens of one of the series (II) contained the C^{14} carbon isotope with a specific activity of approximately 2 microcurie/gram. The amount of bonded carbon in the specimens was 4.8 percent in (I) and 4.7 percent in (II); the amount of free carbon was 0.1 percent; of nitrogen 0.01 percent; of uranium 9.51 percent (I) and 95.2 percent (II). X-ray analysis indicated that all the samples were of the single-phase type with lattice constants equal to a=4.961Å (I) and a=4.958Å (II).

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* Numbers in the margin indicate pagination in original foreign text.

The experiments were conducted using a setup whose heating arrangement is shown in figure 1. The Knudsen tungsten chamber 3 was heated by means of a cylindrical tantalum heater 1, which made it possible to provide for uniform heating along a length of approximately 40 mm. The temperature was measured by means of an optical pyrometer through the opening 6. The temperature was measured with an accuracy of ±5–7°C.

The vaporized material was condensed by copper targets 4 which were subjected to intense cooling; the temperature of the targets did not exceed 50-100°C during the experiments. The design of the setup made it possible to replace targets without disrupting the vacuum. During the experiments the vacuum was maintained at the level of 1×10^{-4}–1×10^{-5} mm Hg. The design of the chamber made it possible to utilize replaceable crucibles made of various materials (Ta, Be, O, W and others) which were placed in the Knudsen chamber.

The area of the effusion opening in the tungsten diaphragm was 1.52×10^{-3} cm^2 in all the experiments; the Clausing correction factor was equal to 1.07 for a diaphragm with a thickness of 0.06 mm. The ratio of the effusion hole area to the chamber area was 0.001. Preliminary experiments conducted with /361 uranium dioxide and uranium carbide showed that when the area of the hole was increased by approximately a factor of 8 to 1×10^{-2} cm^2, the results of the measurements were not affected.

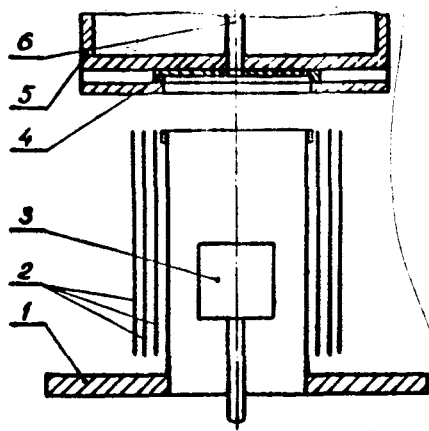Therefore the Rossman-Yardwood correction was not utilized in the computations.

Figure 1. Schematic representation of heating arrangement: 1. tantalum heater; 2. screens; 3. Knudsen chamber; 4. cartridge; 5. cartridge holder; 6. hole for temperature measurement.

The vapor pressure was computed by means of the well-known equation

$$P = G\sqrt{\frac{2\pi RT}{M}}, \qquad (1)$$

where P is the vapor pressure, G is the rate of effusion, M is the molecular /362 weight of the vapor, R is the gas constant, and T is the absolute temperature. The condensation factor for the targets was taken equal to one.

As we can see from figure 1, in our experiments the upper part of the heater served as a reflector for the effusing atoms. Special experiments were carried out to take into account this additional reflection. In these experiments a hollow conic collimator was installed on the heater eliminating the effect of additional reflection from the walls of the heater. In the case of our experiments (with a distance of 115 mm from the center of

TABLE 1. RESULTS OF STUDIES ON THE VAPORIZATION OF URANIUM
MONOCARBIDE.

№	1 Метод исследования	2 Интервал температур, °К	3 Вид зависимости $\lg P(\text{мм}) - \frac{1}{T}$	Теплота[4] сублимации, ккал/моль	5	6 Примечание
1	Кнудсеновский 7	1948 – 2133	$\log P = 21{,}3 - \dfrac{49{,}2\cdot 10^4}{T}$	225	[1]	Испарение из длинного тигля; весовой метод. 10
2	Кнудсеновский 8	1910 – 2660	$\log P_u = 8{,}98 - \dfrac{27{,}8\cdot 10^4}{T}$	126	[2]	–
3	Ленгмюровский 9	2250 – 2524	$\log P_u = 9{,}33 - \dfrac{36{,}9\cdot 10^4}{T}$	168	[3]	Весовой метод
			$\log P_{c_2} = 10{,}48 - \dfrac{36{,}9\cdot 10^4}{T}$	168		11

Key:

1- Method of investigation
2- Temperature interval, °K
3- Form of the relationship log P (mm)-1/T
4- Heat of sublimation, kcal/mole
5- Source
6- Remarks
7- Knudsen
8- Knudsen
9- Langmuir

10. Vaporization from a. long
    crucible; gravimetric method
11. Gravimetric method

the effusion hole of the heater, an internal heater diameter of 38 mm and a cart-ridge diameter of 42 mm) the number of atoms condensating on the target was approximately 0.33 of the total number of effusing atoms.

The radiometric analysis of sputtered targets as well as of α- and β-standards was carried out using scintillation counters and end-window counters. By using monocarbide compounds with inactive (I) and active (II) carbon it was possible to isolate the portion of uranium and C^{14} in the total radiation. The maximum error in the determination of the vapor pressure was approximately 12 percent.

The vapor pressure of the dioxide and of uranium was measured to verify the reliability of results obtained by means of the setup. The experiments were carried out in tantalum crucibles; before the measurements uranium dioxide was fired for a prolonged period of time at a temperature of 2100°C. The results of the measurements taken during heating and cooling showed good agreement. The data are presented in table 2 and in figure 2.

The temperature dependence logP had the form:

$$\log P\,(\text{mm Hg}) = 10.025 - \frac{2.757\cdot 10^4}{T};$$ the heat of sublimation ΔH_T was found to be equal

to 126 kcal/mole.

TABLE 2. VAPORIZATION RATE AND VAPOR PRESSURE FOR URANIUM DIOXIDE

$T°K$	t in seconds	Vaporization rate gram $\times$ cm$^{-2}\times$ sec^{-1}	Vapor pressure in mm Hg
2063	$6.84 \cdot 10^3$	$1.052 \cdot 10^{-5}$	$4.99 \cdot 10^{-4}$
2148	$3.6 \cdot 10^3$	$3.285 \cdot 10^{-5}$	$1.589 \cdot 10^{-3}$
2228	$1.8 \cdot 10^3$	$9.47 \cdot 10^{-5}$	$4.615 \cdot 10^{-3}$
2273	$9 \cdot 10^2$	$1.595 \cdot 10^{-4}$	$7.94 \cdot 10^{-3}$
3308	$6.3 \cdot 10^2$	$2.67 \cdot 10^{-4}$	$1.341 \cdot 10^{-2}$

These data are in good agreement with the results obtained in references 1 and 5.

Table 3 and figure 3 show the results of measuring the partial vapor pressures of uranium and of carbon over uranium monocarbide. The temperature dependences logP(mm Hg) have the form

$$\log \bar{P}_u = 10.054 - \frac{2.809 \cdot 10^4}{T},$$ (2)

$$\log \bar{P}_c = 2.515 - \frac{1.324 \cdot 10^4}{T}.$$ (3)

The partial sublimation heats $(\overline{\Delta H_T})$, computed by the method of least squares, were equal to 128.5 for uranium and 60.6 kcal/mole for carbon. The computations of the partial vapor pressure of carbon were carried out under the assumption that vaporization is monatomic and takes place in accordance with the following formula

$$UC_{solid} \rightarrow U_g + C_g.$$ (4)

The value $\overline{\Delta H_T}$ determined by us for uranium is in good agreement with the results obtained by Alexander and his co-workers (ref. 2); however, the absolute values of the vapor pressure differ by approximately 1 order of magnitude. In references 1 and 3 the gravimetric method was used to determine the total values of sublimation heats for the compounds rather than the partial sublimation heats. If we assume that $\Delta H = \Delta H_u + \Delta H_c$, then the values obtained by us for the sublimation heat of uranium
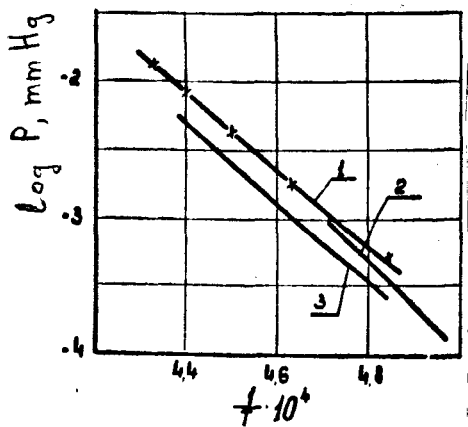

Figure 2. Variation in the vapor pressure of uranium dioxide as a function of temperature: 1--our data; 2--the results of investigations carried out in reference 1; 3--results of investigations carried out in reference 3.

TABLE 3. THE VAPORIZATION RATE AND VAPOR PRESSURE OF
CARBON OVER URANIUM MONOCARBIDE.

$T^\circ K$	t in seconds	The amount of vaporized materials, in grams	Vaporization rate, gram x $cm^{-2} x sec^{-1}$	Vapor pressure in mm Hg
1878	$4,260 \cdot 10^4$	$1,057 \cdot 10^{-5}$	$1,623 \cdot 10^{-7}$	$3,482 \cdot 10^{-5}$
1993	$4,896 \cdot 10^4$	$2,161 \cdot 10^{-5}$	$2,905 \cdot 10^{-7}$	$6,240 \cdot 10^{-5}$
2118	$1,710 \cdot 10^4$	$2,034 \cdot 10^{-5}$	$7,830 \cdot 10^{-7}$	$1,781 \cdot 10^{-4}$
2283	$9.0 \cdot 10^3$	$2,507 \cdot 10^{-5}$	$1,834 \cdot 10^{-6}$	$4,335 \cdot 10^{-4}$
5358	$1,980 \cdot 10^3$	$1,137 \cdot 10^{-5}$	$4,156 \cdot 10^{-6}$	$1,0 \cdot 10^{-3}$

carbide are 199.1 kcal/mole, which in absolute value is greater than the values obtained in reference 3 and less than the results in reference 1 (see table 1).

We should also like to note that the computations of $\bar{P}c_3$ by means of the formula

$$UC_{solid} \rightarrow U_g + C_{3_g},$$ (5)

adopted in reference 3 will not introduce any corrections to the present values of ΔH_T; only the absolute value of the partial pressure of carbon vapor uranium

monocarbide will be reduced by a factor of $\sqrt{3}$. Future mass-spectrometric investigations must refine the monatomic or polyatomic nature of carbon vaporization from uranium carbide.

By using the results which have been obtained on the partial pressures of carbon and uranium over uranium monocarbide, we computed some of the thermodynamic characteristics. The following expressions were obtained for the variation of free partial molar energy of sublimation

(6)

$$\overline{\Delta F}_{T(u)} = 128\,500 - 32{,}8\,T,$$

$$\overline{\Delta F}_{T(c)} = 60\,600 + 1{,}67\,T.$$ (7)

The values of partial molar sublimation entropies were ± 32.8 and -1.67 cal/mole, $^\circ C$ for uranium and carbon respectively. By taking into account the sublimation heat (ΔH_T^o) of uranium which, according to data in reference 6, is

equal to 105.6 kcal/mole, the relative partial molar sublimation heat (ΔH_T^M) turned out to be equal to approximately 23 kcal/mole.

The partial sublimation heat of uranium reduced to $298^\circ K$ was computed by the well-known equations:

$$\Sigma = \frac{\Delta H_{298}}{T} + \mathcal{J},\tag{8}$$

$$\Delta H_{298} = \Delta\left[T\left(\frac{F_T^0 - H_{298}^0}{T}\right)\right] - 4.575\, \log\, P,\tag{9}$$

where $\Sigma = 4.75\, \log P - \Delta Cp\log T$; $\Delta_0 Cp$ is the difference of specific heats for the /365 reaction $UC_{solid} = U_g = C(\text{graphite})$; $\Delta\left[T\left(\frac{F_T^0 - H_{298}^0}{T}\right)\right]$ is the difference of the reduced thermodynamic potentials for the same reaction: $\mathcal{J}$ is the integration constant.

The values of specific heat and of the reduced thermodynamic potentials for graphite and for gaseous uranium were taken from reference 7 while the following relationship was used for the specific heat of uranium moncarbide:

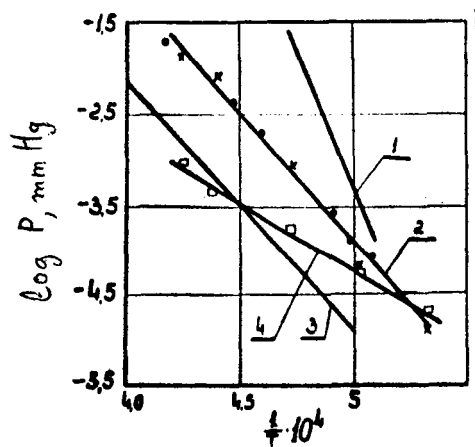$$C_p = 13.40 + 1.02 \cdot 10^{-3}\, T - 1.46 \cdot 10^5\, T^{-2},\tag{10}$$

Figure 3. The variation in the vapor pressure of uranium monocarbide as a function of temperature: 1. the results obtained in reference 1; 2. our data on the partial vapor pressure of uranium (specimens of I,X, specimens of series II); 3. results obtained in reference 2; 4. our data on the partial vapor pressure of carbon.

This relationship was proposed by experts on thermodynamics at the Vienna conference (ref. 8).

The value of the reduced thermodynamic potential for the carbide was computed in the conventional manner; the value of S_{298} was assumed to be equal to 14.2 (ref. 8). Computation by means of the second law presented in reference 8 under the assumption that $\Delta C_p = \text{const}$[1] yielded a value of 132.6 kcal/mole for ΔH_{298}. Calculations carried out by means of the third law yielded a value of $\Delta \bar{H}_{298} = 123.1 \pm 1$ kcal/mole.

The difference in the results of calculations carried out by means of the II and III laws is observed rather frequently in experiments on vaporization (for example, reference 9). This is explained both by the systematic errors in experiments on vaporization as well as by the fact that the data used in the computation of reduced thermodynamic potentials are not entirely accurate. If

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[1]For the investigated temperature range the difference in specific heats varies from 2.7 to 2.92. It was assumed that $\Delta C_p = 2.8$ in the calculations.

according to data in reference 10 we assume that the heat of vaporization of uranium (ΔHO_{298}) is equal to 115.2 kcal/mole, then the heat of formation for uranium carbide at 298°K is equal to 17.4 and 7.9 kcal/mole when computed by the II and III laws respectively. The latter value of ΔH_{298} is clearly below

that recommended by the values of the heat of formation UC(-21.7±1.0 kcal/mole (ref. 8)). In addition to the factors mentioned above which complicate the precise determination of $\overline{\Delta H}_{298}$ and hence of the heat of formation, we can also

state that calculations of this type could be carried out more accurately if we were to consider the evaporation scheme defined by equation (4) or equation (5). However, the absence of information on the nature of carbon vaporization from uranium monocarbide and the inadequate accuracy associated with the vaporization of pure carbon (for example, reference 4) make it possible to carry out these calculations with sufficient accuracy. We can see from figure 3 that, from the standpoint of absolute value, at all investigated temperatures with the exception of 1878°K, the vapor pressure of uranium is higher than the vapor pressure of carbon. It is expedient to evaluate the atomic ratio of carbon to uranium in the vapor stage. Figure 4 shows the temperature variation in the parameter λ which is equal to the ratio G_cM_u/M_cG_u , where G_i are the partial

vaporization rates of carbon and uranium, while M_i are the atomic weights. As follows from these data, up to a temperature of approximately 2100°K we observe primarily the vaporization of carbon atoms; above this temperature the uranium monocarbide is depleted of uranium and enriched with carbon. This situation is also noted in references 3 and 11, where it has been established that prolonged holding in vacuum at temperatures 2250-2540°K leads to the enrichment of the carbide with carbon up to the composition $UC_{1.1}$.

The congruent vaporization of uranium monocarbide without a charge in composition (λ=1) is observed only at a single temperature. This is quite understandable as we note that the partial heats of sublimation for uranium and carbon differ by approximately 70 kcal/mole. In this connection the results obtained in the investigation of uranium monocarbide vaporization by the Langmuir (ref. 3) method appear to us to be incorrect. It is of interest to study the kinetic laws associated with the variation in the composition of uranium carbide over a wide temperature range.
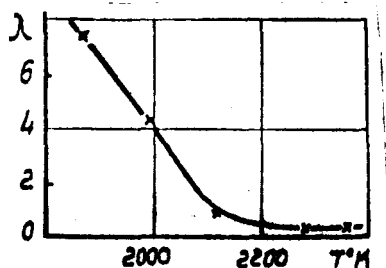

Figure 4. Temperature variation of parameter λ (relationship of quantity of carbon atoms to quantity of uranium atoms in gas phase).

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